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Energetics of CO-NO reactions on Pd-Cu alloy particles

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Abstract : The bond-order conservation-Morse potential model (BOCMP) has been used to study the CO-NO reaction on Pd-Cu alloy particles having total number of atoms per particle in the range of 200–1300. Monte Carlo simulation has been performed to find the surface composition of the particles. Cu has been found to segregate to the surface for particles of all sizes—the extent of segregation slowly increasing with particle size. Activation energy analysis shows that CO_2 formation is the rate-limiting step for the overall CO-NO reaction. The most active sites are found to be the three-fold hollow adsorption sites with three Cu nearest neighbours, and the adsorption sites with two Cu atoms and one Pd atom as nearest neighbours.

Keywords : Adsorption, (BOCMP) model, segregation, activation energy, CO oxidation, NO reduction

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1. Introduction

Automobile exhaust gases have a composition of approximately 75% carbon monoxide (CO) and 10% nitrogen oxides (NO_x), —the rest consisting of a large number of unburnt hydrocarbons and some sulphur dioxide *etc* [1–3]. Efficient pollution control would mean almost total conversion of CO (by oxidation) to CO_2; reduction of NO to N_2 and oxidation of the hydrocarbons to CO_2 and H_2O. Intensive research over last two decades on suitable catalysts for simultaneous oxidation of CO and hydrocarbons on one hand and the reduction of NO on the other has led to the development of a near-ideal catalyst, namely, Pt-Rh/ceria [1–3]. However, in view of the excessive use of Rh and Pt in the auto-catalytic converters the world stock of Rh and Pt is fast dwindling and it is important therefore to find some alternative but cost-effective catalysts. Pd is a good oxidation catalyst and Cu is a good NO reduction catalyst since Cu dissociates NO very efficiently. It is the purpose of this present work to study the adsorption, segregation and catalytic properties of these metals and their alloys for CO oxidation and NO reduction.

A full investigation on the CO-NO reaction on a catalyst surface would require the knowledge of the possible reaction steps, the heat of adsorption of the reactants like CO, NO, O, CO_2 *etc.*, activation energy for dissociation of NO, activation energy for recombination of CO and O to form CO_2 and the activation energy for formation of N_2. In addition, for supported bimetallics one should also have a knowledge of the surface composition of the catalyst particles. In section 2 we present the results for surface composition of Pd-Cu particles obtained by Monte-Carlo simulation. In section 3 we discuss the possible reaction steps and the rate-limiting step on the basis of heat of adsorption and the activation energies for various steps. These are done on the basis of bond-order conservation model of Shustorovich [4]. In section 4 we calculate the activity of the Pd-Cu bimetallics as a function of the particle size. Also we discuss the role of local surface order on the activity.

2. Segregation in Pd-Cu bimetallic particles

The bimetallic particles, generally used as catalysts, have diameters in the 2 nm–5 nm range having the number of atoms per particle in the range of 200–5000. It is a general property of the bimetallic alloys that atoms of one constituent may preferentially enrich the surface. We use here the theoretical Monte-Carlo technique to calculate this surface composition of Pd-Cu particles. For simplicity we consider the *fcc* cubo-octahedron shaped particles. This is because, thermodynamically for particles of 2 nm–5 nm size cubo-octahedron is the most stable geometry. The details of the Monte-Carlo technique used in this calculation is described elsewhere [5]. Essentially, the method relies on finding the most stable configuration energy with respect to switching the A and B atoms of an alloy A–B. For the bond energy between two nearest neighbour atoms j and k with the coordination n and m respectively we use the formula

$$E_{jk} = [\omega_{jk}/Z] + [E_c^j(n)/n] + [E_c^k(m)/m]$$

where j, $k = A$ or B atom and $\omega_{jk} = 0$ if $j \neq k$. The first term, known as the interchange energy is obtained from the molar excess heat of mixing [5]; the second and third terms denote the cohesive energy per bond of the j-th atom having n coordination and the k-th atom having m coordination respectively. For this calculation the interchange energy is found to be –0.0197 eV. The cohesive energy per bond is calculated from the surface-modified pair potential formula is given in Ref. [6].

The results presented here correspond to the $Pd_{50}Cu_{50}$ composition in the bulk. We have calculated the surface composition of particles with 201, 586 and 1289 atoms. The dispersion (D) and the fraction of surface sites covered by Pd and Cu atoms are presented in Table 1. N_T is the total number of atoms in a particle. X_s is the surface concentration. It may be noted that for 50% Cu concentration in the bulk the surface concentration of Cu in the surface is much higher for all the particles. The surface composition as obtained by MC

simulation for a typical 586-atom particle is shown in Figure 1. The shaded atoms are Cu atoms. It may be noticed that the Cu atoms occupy the corner and edge sites of the particle.

Table 1. Site statistics of *fcc* cubo-octahedron Pd-Cu particles

$N_T \rightarrow$	201	586	1289
D	0.6	0.46	0.37
X_s (Pd)	0.35	0.335	0.31
X_s (Cu)	0.65	0.665	0.69

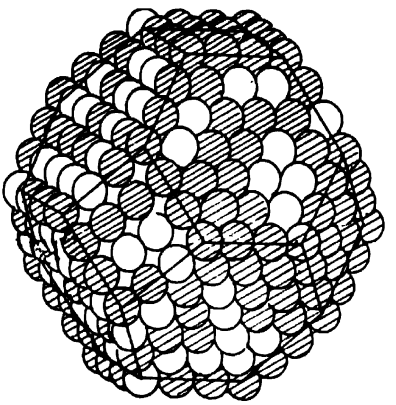

Figure 1. Surface composition of 586-atom Pd-Cu cluster

The Monte-Carlo simulation also gives the average number of surface Pd (and Cu) neighbour per surface Pd (and Cu) atom. These numbers are useful to study the role of surface ordering in catalytic activity.

3. Surface reactions and activation barriers

The overall reaction step may be given as

$$CO_s + NO_s \rightarrow CO_2 + \tfrac{1}{2}N_2 \tag{1}$$

where the suffix '*s*' denotes the components in the adsorbed phase. But in reality it is the intermediate steps which are important and should be considered seriously to find the rate-limiting step. The intermediate steps are the following :

$$CO_g \rightarrow CO_s, \tag{2}$$

$$NO_g \rightarrow NO_s, \tag{3}$$

$$NO_s \rightarrow N_s + O_s, \tag{4}$$

$$CO_s + O_s \rightarrow CO_2, \tag{5}$$

$$N_s + N_s \rightarrow N_2, \tag{6}$$

$$NO_s + N_s \rightarrow N_2O_s, \tag{7}$$

$$N_2O_s \rightarrow N_2 + O_s. \tag{8}$$

The expressions (2) and (3) denote the adsorption of the molecules from the gas phase. On the basis of available experimental adsorption energies and the bond-order conservation —Morse potential model [4] the activation energy for various steps may be found. The rate of adsorption from gas phase depends on the sticking coefficients of the relevant molecules. But, once the molecules are adsorbed further reactions take place with activation energy as given in Table 2. It may be mentioned here that since experimental adsorption energies for particles are rare we calculate first the activation energies for single crystal (111) surface of the metals. For particles with number of atoms larger than 200 the average adsorption energy of atoms and molecules and the activation energies for various steps may then be calculated by a statistical analysis [7].

Table 2. Activation energy (in k cals/mole).

Metal	Pd (111)	Cu (111)
$NO_s \rightarrow N_s + O_s$	9 1	1.0
$CO_s + O_s \rightarrow CO_2$	24	20
$N_s + N_s \rightarrow N_2$	43	25
$NO_s + N_s \rightarrow N_2O_s$	25.7	12 5
$N_2O_s \rightarrow N_2 + O_s$	-ve	-ve

From the results presented in Table 2 the following conclusions are drawn. It may be noted that Cu dissociates NO very fast. Formation of N_2 from two adsorbed N atoms requires higher activation energy than formation of N_2O which subsequently dissociates spontaneously into N_2 and O. However, in view of the alloy segregation property since 65–70% surface sites are occupied by Cu atoms surface properties of Cu will control the overall surface reactions. In this respect since CO_2 formation on Cu has higher activation energy, this CO_2 formation is most likely to be the rate-limiting step. For Pd sites also the activation barrier for CO_2 formation is close to the activation barrier for N_2O formation. Thus in all likelihood for the Pd-Cu single crystal alloy CO_2 formation from adsorbed CO and O is the rate-limiting step. From the energetics of adsorption on particles (since adsorption energy varies very slowly with N_T for $N_T > 200$), the rate-limiting step is found to be the same for Pd-Cu particles.

4. Activity of Pd-Cu bimetallic particles

The activity of Pd-Cu particles for the CO oxidation reaction is expressed as

$$'a' = \sum A p_i (X_s) \exp\left(-E_i^* / RT\right) \tag{9}$$

where A is a constant depending on the collision frequency of the gas-solid system $p_i (X_s)$ is a steric factor and is a function of the surface geometry of the system. It denotes the probability to find a chemisorbed bond with i Pd and $3\text{-}i$ Cu nearest neighbours.

Usually, $p_i(X_s)$ is given by the binomial distribution

$$p_i(X_s) = [3!/i!(3-i)!]X_s^i(1-X_s)^{3-i} \tag{10}$$

The number 3 comes into picture since the adatoms are assumed to occupy the centre positions (sites with three-fold symmetry in the (111) surface of *fcc* lattice). The calculated activity for CO oxidation is shown in Figure 2. The activity increases linearly with increase

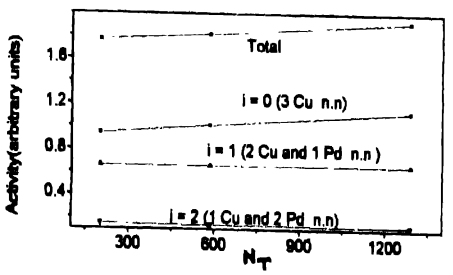

Figure 2. Activity of Pd-Cu alloy for CO oxidation and contribution from different i values (Eqn 9)

in the size of the particles. This is because, Cu segregates increasingly with particle size to the surface; and Cu has a lower activation barrier for CO oxidation than Pd. Therefore, with increase in particle size the activity increases. The main contribution to the activity comes from adsorption sites with 3 Cu sites as nearest neighbours and adsorption sites with 2 Cu and one Pd atom as nearest neighbours.

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